Simple conditions have been developed for the effective synthesis of 7-hydroxy- and 5,7-dihydroxyisoflavones and also of 3-aryloxy-7-hydroxychromones. The advantages and disadvantages of alternative pathways of the synthesis of the compounds are discussed. A method is proposed for the synthesis of isoflavones and 3-aryloxychromones which permits a considerable simplification of the preparation of compounds of these series in the necessary amounts.

LITERATURE CITED


NATURAL ANTIOXIDANTS.

FURANOEREMOPHILANES FROM Cacalia ROOTS

N. P. Krasovskaya, N. I. Kulesh, and V. A. Denisenko

Sesquiterpene compounds of the furanoeremophilane series have been isolated from extracts of the roots of Cacalia sp. growing in the Soviet Far East. The presence of antioxidant and antiradical activities in two representatives of the series has been established.

The present paper, which continues a cycle of investigations directed to the search and characterization of antioxidants from plants of the Far East [1-5] reports the results of the isolation of nonpolar antioxidants and the determination of their structures.

Wide screening among herbaceous plants has revealed a number of taxons producing such compounds. Included among them were several species belonging to the genus Cacalia, family Asteraceae.

Plants of the genus Cacalia have been studied chemically very thoroughly. Romo et al. [6, 7] were first to isolate from the roots of the shrub C. decomposita A. Gray a group of sesquiterpene compounds of the furanoeremophilane series which they called cacalol, cacalone, and decompostin. Later, British and Japanese investigators studying seven representatives of the genus Cacalia isolated from the roots more than 30 compounds that were derivatives of cacalol, cacalone, and decompostin [8-15].

We have studied extracts of the roots of four species of Cacalia growing in the Far East: C. auriculata DC., C. hastata L., C. robusta Toim., and C. aconitifolia Bunge. From hexane extracts of C. auriculata (Table I) we have isolated cacalol, cacalone, and 6β-propionyloxy-1,10-furanoeremophil-9-one, which has been detected previously in the roots of C. decomposita [6, 7] and C. adenostyloides [15].

Hexane extracts from C. robusta and C. hastata proved to be qualitatively identical. A hexane extract of Cacalia aconitifolia proved to be completely different. No compounds of the furanoeremophilane series were detected in it. Column and preparative chromatography with subsequent mass spectroscopy of the fractions showed only the presence of 6α-sitosterol and of oleanolic acid acetate, which were identified by comparison (TLC, melting points) with authentic samples.

Thus, the hypotheses put forward previously that from their botanical characteristics the species C. aconitifolia cannot be assigned to the genus Cacalia [16, 17] are confirmed by the chemical facts given above, although ethyl acetate extracts of all the plants studied proved to be identical in qualitative composition and contained among the main phenolic components caffeic acid and its derivatives.

Below, we give the activities of the furanoeremophilanes isolated from the roots of Cacalia sp. (a – at an inhibitor concentration of 0.03 mg/ml; b – 0.10 mg/ml):

<table>
<thead>
<tr>
<th>Compound</th>
<th>Antioxidant activity (in comparison with Ionol)</th>
<th>Antiradical activity (in comparison with α-tocopherol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cacalol</td>
<td>0.28a, 0.31b</td>
<td>0.27</td>
</tr>
<tr>
<td>Cacalone</td>
<td>0.02a, 0.03b</td>
<td>0.02</td>
</tr>
<tr>
<td>Cacalol acetate</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>6β-Propionyloxy-1,10-furanoeremophil-9-one</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>O-Methylcacaioene</td>
<td>None</td>
<td>None</td>
</tr>
</tbody>
</table>

As we see, cacalol possesses a fairly high antioxidant and antiradical activity while cacalone is only slightly active.

We have characterized the activities of the caffeic acid derivatives previously [4].

EXPERIMENTAL

For TLC we used Silufol plates, while column chromatography was carried out on KSK silica gel. Chromatograms were run in the toluene-acetone (95:5) and benzene-methanol (4:1) systems; melting points were determined on a Boetius stage (and are uncorrected); optical rotations were measured on a Perkin-Elmer 141 polarimeter; NMR spectra were taken on a Bruker WM-250 spectrometer with working frequencies of 250 MHz for 1H and 62.9 MHz for 13C. Mass spectra were obtained on a LKB-9000S spectrometer by the direct introduction of the sample into the ion source at energies of 15 and 70 eV. UV spectra were taken on a Cary-Varian 219, in methanol. GLC was conducted on a GC-5AP instrument (Shimadzu) with a flame-ionization detector (3% of OV-1, program 80-300°C at 6°C/min).